Supramolecular Electro- and Proto-Photoswitch

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(Received December 9, 1998; CL-980909)

The fluorescence from a zinc-tetraphenylporphyrin–4-(phenylazo)pyridine supermolecule is switched on/off responding to external redox or (de)protonation stimuli, exemplifying a non-covalent approach to construct supramolecular photoswitches.

Molecular photonics/electronics devices are based on electronic communication and its switching among suitably organized photo/electro-active molecule-based species. A luminescence switch is important, since, for one, it may be used to control pursuing energy/electron transfer processes.[1] Such devices are constituted by a light-emitting center and a quencher linked by a spacer.[2,3] Redox reactions of the quencher may effect interconversion between a luminescent state and a non-luminescent state. Widely studied photo-induced electron transfer sensors are also made up of an emitter–quencher motif, but the stimulus is the presence of specific chemical species.[4] While most of such conjugated molecules so far involve a covalent spacer linking an emitter and a quencher, the use of non-covalent interactions to assemble multi-component complexes has wider scope.[2,4-7] Here we describe a supermolecule, in which a light emitting center (Zn-tetraphenylporphyrin; ZnTPP) is connected with a quenching component (4-(phenylazo)pyridine; PhNNPy) via a labile non-covalent interaction (axial coordination), that functions as an electron- and proton-responsive photoswitch.

The magnitudes of ^{1}H NMR limiting complexation-induced upfield shifts of PhNNPy, determined by assuming 1:1 equilibrium adduct formation with ZnTPP, establish that the pyridine-N coordinates to ZnTPP as shown in the insert of Figure 1.[8] In accordance with the adduct formation via the axial coordination, porphyrin Q bands exhibit a characteristic red-shift showing isosbestic points, from which the association constant is derived as 3200 M^{-1} (1 M = 1 mol dm^{-3}) in 1,2-dichloroethane at 25 °C, conditions used throughout the present experiments. The integrated fluorescence intensity from ZnTPP diminishes upon successive addition of PhNNPy, which is plotted in Figure 1. The figure also shows the relative amount of free ZnTPP obtained from absorption measurements. The coincidence of these curves is indicative of nearly quantitative intracomplex quenching as well as negligible diffusional quenching in the concentration range, showing the effectiveness of this quencher, which is not attainable by previously reported imide derivatives.[9] Thus it is shown that the axial coordination is proven to be useful in constructing an emitter-quencher supermolecule, in which the quenching is very effective.[10]

If the quenching of ^{1}ZnTPP* by PhNNPy$^-$ is ineffective, which is expected if the quenching is due to electron transfer, electrochemical reduction of PhNNPy should restore the fluorescence from the supramolecular complex. When ZnTPP is alone in solution, a large fluorescence is observed (dot in Figure 2). Addition of PhNNPy to this solution results in the decrease of the fluorescence (solid). The remaining fluorescence is due to free ZnTPP as is apparent from the peak wavelengths. Potentiostatic one-electron reduction of PhNNPy causes an increase in the fluorescence intensity up to ca. 75% of the initial intensity (dash).[11] The red-shifted fluorescence indicates that it emanates from the complex, ZnTPP—PhNNPy$^-$. Re-oxidation back to neutral PhNNPy causes the fluorescence to decrease again. The two pairs of peaks (dash/dot) show the presence of fluorescence from free ZnTPP and remaining ZnTPP—PhNNPy$^-$ at the final stage of the oxidation. During these redox reactions, absorption shows a little change in a way indicating that the anion PhNNPy$^-$ has higher affinity toward ZnTPP than the neutral species. This is also noted from the decrease in the otherwise increasing fluorescence around 590 nm when being reduced.

Since the emitter-quencher supermolecule is constructed via a labile reversible bond, we reasoned that the association and

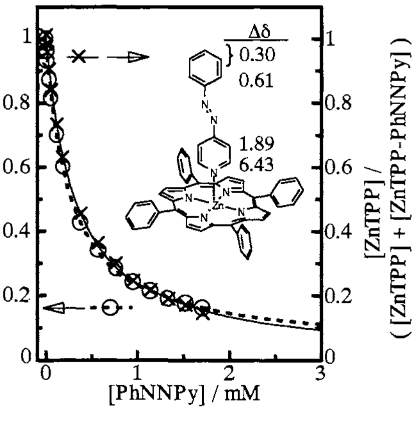

Figure 1. Integrated fluorescence intensity (circle and dotted line; left axis; λ_{ex}: isosbestic 555 nm) and the relative amount of free ZnTPP (cross and solid line; right axis) against PhNNPy concentration (10 μM ZnTPP, 1,2-dichloroethane, 25 °C). Inset: The limiting complexation induced ^{1}H NMR upfield shifts in $CDCl_3$ and the structure of ZnTPP-PhNNPy.

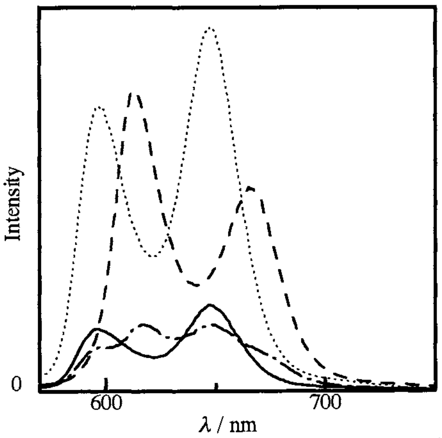

Figure 2. Fluorescence spectra of 10 μM ZnTPP in 1,2-dichloroethane containing 0.1 M tetrabutylammonium perchlorate (dot). To this solution, 1 mM PhNNPy was added (solid), reduced (dash), and re-oxidized (dash/dot).

dissociation process may also be used to effect fluorescence switching.[12] The association and dissociation processes can be monitored by absorption spectra step by step as shown in Figure 3. Upon addition of PhNNPy (1 mM) to ZnTPP, the spectrum in this case shows that 23% of ZnTPP is complexed, the fluorescence is decreased to 24% correspondingly. Addition of dichloroacetic acid (10 mM) to this solution causes protonation of the pyridine-N in PhNNPy,[13] depriving of its coordination ability. Consequently, ZnTPP is freed from the complex and the fluorescence restores almost up to the original intensity. Further addition of excess K_2CO_3 to this mixture, followed by stirring and filtration, deprotonates $PhNNPyH^+$ to give the neutral species and the coordination restored, and then the fluorescence becomes quenched again. The repetition of this cycle is demonstrated in the inset of Figure 3.[14]

Figure 4 summarizes the reversible switching processes described herein.[15] The fluorescence from ZnTPP is turned on/off by two kinds of external stimuli. One is the redox reaction of the control unit (quencher) within the supramoleclar complex. The other is protonation/deprotonation which effects dissociation/ association of the supramolecular complex. The latter mode of operation is unique to such a system that the components are connected via a reversible intermolecular bond.

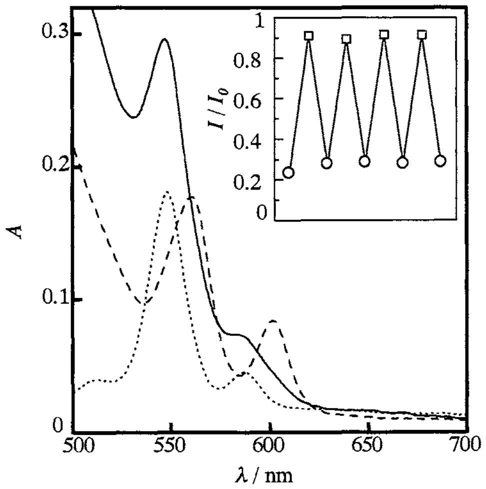

Figure 3. Absorption spectra of 10 μM ZnTPP in 1,2-dichloroethane (dot). To this solution were added 1 mM PhNNPy (dash), 10 mM dichloroacetic acid (solid), and excess K_2CO_3 (nearly identical to dash). Inset: Relative integrated fluorescence intensity upon repeated addition of the acid (square) and base (circle).

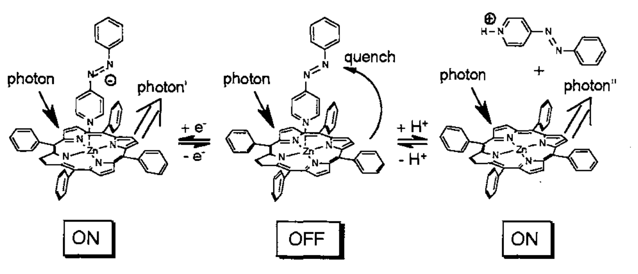

Figure 4. The mode of operation of the supramolecular electro- and proto-photoswitch.

This work was supported by Nissan Science Foundation, Foundation Advanced Technology Institute, and the Ministry of Education, Science and Culture.

References and Notes

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10 The quenching may be either due to electron or singlet energy transfer. Electron transfer is energetically possible, since the redox potential of the singlet excited state of ZnTPP (-1.63 V vs Fc/Fc^+) is more negative than that of PhNNPy (-1.84 V).

11 Constant potential at -1.7 and -0.2 V was applied for reduction and oxidation, respectively, to a solution of 10 μM ZnTPP and 1 mM PhNNPy in 1,2-dichloroethane containing 0.1 M tetrabutylammonium perchlorate in a N_2 bubbled fluorescence cell with a Pt mesh electrode. Reference and counter electrodes were Ag/Ag^+ and Pt, respectively. The potential was applied until no more spectroscopic change was observed. Completion of the redox reaction was difficult due to the bulk nature of the cell.

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14 The acid and base do not have any direct effect on ZnTPP or its fluorescence, except that prolonged exposure to acid causes demetallation of ZnTPP.

15 The effect of *cis-trans* isomerization of PhNNPy was also investigated. However, no indication was obtained concerning changes either in coordination or quenching behaviour concomitant with the isomerization reaction.